

10099310 082802

JC20 Rec'd PCT/PTO 27 MAR 2002

EXPRESS MAIL LABEL NO.: EJ083185194US

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

P1999S008

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/089310

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

INTERNATIONAL APPLICATION NO.

EP00/10186

INTERNATIONAL FILING DATE

17.10.00

PRIORITY DATE CLAIMED

29.10.99

TITLE OF INVENTION

JET FUELS WITH IMPROVED FLOW PROPERTIES

APPLICANT(S) FOR DO/EO/US

Simon Christopher Peter Ashton

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is the **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is the **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application number PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☒ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

PCT Request; International Application Number & International Filing Date; Receipt of Record Copy; International Search Report;
International Application to the Designated Offices; International Application as Published; Written Opinion; Response to Written Opinion;
International Preliminary Examination Report



27810

PATENT TRADEMARK OFFICE

Joseph J. Allocca
Joseph J. Allocca, Reg. No. 27,766
Attorney for Applicants

JET FUELS WITH IMPROVED FLOW PROPERTIES

This invention relates to jet fuels, especially kerosine based fuels, with improved cold flow properties.

It is well known that liquid hydrocarbons change phase and tend to deposit solid crystals of wax at low, freezing temperatures. However, the nature of the crystals and extent to which deposition occurs depends very much on the molecular structure of the liquid hydrocarbons and their solubility. Thus, the freezing points are usually the highest for high molecular weight n-paraffins, relatively lower for branched chain paraffins and are the lowest for hydrocarbons rich in naphthenes and aromatics. Since the major component of jet fuel come from fractions forming the kerosine boiling range, the amount of high molecular weight n-paraffins in this fraction dictate the freezing point of jet fuels. The components responsible for controlling the freezing point in jet fuels are generally in the high-boiling end of such a fraction. Hence, the final boiling point of the fractions of kerosine which are or can be used as jet fuels is governed by considerations of the freezing point of a given fraction. Most jet fuels are straight-run distillates. The composition of the crude feed being subjected to distillation determines the composition of the fraction boiling within the kerosine boiling range and hence the freezing point of the jet fuel.

Hitherto, in some refineries, some of the aforementioned problems have been mitigated by chemically adjusting the composition of some of these fractions used in jet fuels by processes such as eg hydrocracking. In the latter process, the heavier paraffinic and aromatic fractions are broken down into relatively smaller molecules and are hydrogenated at the same time. This is particularly the case with long-chain paraffins which are cracked into smaller molecules having a molecular weight within the desired range and the process simultaneously results in branched chain molecules being formed. Thus, the process gives rise to products having much lower freezing points than that of the original distillate prior to hydrocracking.

It has also been suggested in EP-A-0282342 that cold-flow properties of fuels can be improved by adding to said fuel a minor proportion of a copolymer of (i) an α -olefin 2-17 carbon atoms per molecule or an aromatic substituted olefin having 8-40 carbon atoms per molecule and (ii) a mono- or a di-alkyl ester selected from fumarates, itaconates, citraconates, mesaconates, trans- or cis-glutaconate in which the alkyl group

has 8-23 carbon atoms. However, these are believed not to be adequate to meet proposed and future legislation with respect to freezing points of fuels.

Whilst the methods currently being used meet the legislation as it stands at present, jet fuels are uniquely likely to be exposed to very low temperatures, especially when flying at high altitudes or when they are on long-haul flights. Other aspects affecting the freezing point of fuels include, flight time, altitude, ambient air temperature, airspeed, fuel pickup temperature, and airframe design which determines the heat transfer characteristics. In the latter context, risk of freezing is also greatest at wing tips, where the highest surface to fuel volume ratio occurs. Under these conditions, the fuel is susceptible to deposition of wax crystals due to insufficiently low freezing points and consequently, may result in problems of pumpability with catastrophic consequences. In order to avoid such incidents, ASTM D2386 has laid down a relationship between the freezing point of jet fuels and pumpability. According to this standard, the minimum temperature at which jet fuel will still flow can vary from 1-10°C below the freezing point. Thus, this definition is believed to be insufficient, if it becomes necessary for the jets to operate at or near the freezing point. The currently accepted standard according to DEF STAN 91-91/1 is for jet fuels to have a freezing point at or below -47°C, which is considered to be reasonably safe with respect to operational needs.

Furthermore, it is also in the interests of the producers and suppliers of jet fuels to maximise the fraction which can be classed as the kerosine boiling range thereby maximising the yield of jet fuel that can be obtained by distillation of a given crude oil. The dependency of the yield of the desired jet fuel fraction from a given crude oil varies with the origin of the crude. Hence, freezing point is a useful guide for determining whether a given crude is a commercially viable source of straight-run distillates which can be used as jet fuels.

As mentioned previously, various methods have been tried to mitigate the risk of fuels cooling down to deposit wax crystals and thereby making it difficult to pump thereby causing blockage of fuel filters or even, in some instances causing solidification of the fuel in the storage tanks themselves. One such method is, for instance, heating the fuel prior to the LP fuel filter to ensure that the fuel temperature is at least 3°C above the freezing point of the fuel. More recently, use of chemical additives to depress the freezing point of such fuels has also been considered. However, the fuel specification for

both civil and military aircraft (as laid down by DEF STAN 91-91) is very stringent and long term testing is needed before any of these can be allowed to be used. For instance, the only fuel containing up to 50% synthetic material and is approved by DEF STAN 91-91-3 is a jet fuel produced by Sasol. Whilst a number of other additives have been
5 allowed, such as eg antioxidants, static dissipators, metal deactivators, lubricity improvers, icing inhibitors and thermal stability improvers, none has been approved hitherto for depressing the freezing point of such fuels.

It has now been found that the freezing point of jet fuels can be depressed well
10 below the minimum levels specified in DEF STAN 91-91/1 by blending therewith a fraction from the distillation process of petroleum crudes.

Accordingly, the present invention is a jet fuel blend comprising a major amount of a kerosine fraction boiling within the range of 140° to 250°C and a minor amount of a naphtha fraction produced by the catalytic cracking of heavy gas oil (hereafter "HCCN")
15 which has a distillation range of $T_5 = 165^\circ\text{C}$ to $T_{95} = 210^\circ\text{C}$ and an aromatics content of at least 50 % by volume such that the resultant jet fuel blend has a freezing point below that of the kerosine prior to blending.

The kerosine fraction forming the major component of such jet fuel blends suitably has a boiling range of $T_5 = 145^\circ\text{C}$ to $T_{95} = 248^\circ\text{C}$, preferably a range of $T_5 = 150^\circ\text{C}$ to $T_{95} = 245^\circ\text{C}$. The amount of the kerosine fraction in the jet fuel blend of the present invention is suitably greater than 75% by volume, preferably in the range from about 80-99%, more preferably from 85-95% by volume of the total blend comprising the
20 kerosine fraction and the HCCN.

The HCCN is a relatively light fraction derived by catalytic cracking of the so-called gasoil fraction during the refining of petroleum crudes. The catalytic cracking of the gasoil fraction to obtain HCCN can be carried out by any of the known conventional
30 catalytic cracking methods. Such methods are well known in the art and are described in detail for instance by Keith Owen and Trevor Colley in "Automotive Fuels Reference Book", Second Edition, published by the Society of Automotive Engineers, Inc, Warrendale, PA, USA (1995). Specifically reference is made to Chapter 3 of this textbook at pages 29-49, Chapter 16 at pages 419-469 and 865-890, the latter pages forming
35 Appendix 12 which is a 'Glossary of Terms'. The HCCN fraction is substantially

unhydrotreated, ie it has not been subjected to hydrotreating and has a boiling range of $T_5 = 165^\circ\text{C}$ to $T_{95} = 210^\circ\text{C}$. The HCCN has an aromatic content of at least 50% by volume, suitably from 50-75% by volume and preferably from 60-75% by volume. The blend of the kerosine fraction and the HCCN is suitably such that the total aromatic content of the blend is in the range from 15-25% by volume of the total blend. The amount of HCCN required to form such blends is suitably from 0.5 to 15% by volume of the blend, preferably from 2.5 to 10% by volume of the total blend.

The freezing point of such a blend can be determined by a number of methods. This can be done, for instance, by detecting the cloud point of blend using optical sensors or by absorption of light through a sample of the blend. It can also be determined by monitoring the change in cooling rate of the blend as energy is absorbed in the formation of, or released in the dissolution of wax crystals. The latter method can be carried out using a freeze point analyser (Models FPA-30, FPA-50 and FPA-70, marketed by Phase Technology Inc). Alternatively, the freezing point, aromatics and saturated content can be determined using near infra-red (NIR) methods. Yet another method for determining freezing points is the so-called cold-filter plugging point method (hereafter "CFPP"). In another method, known as the Setpoint Detector method (ex Stanhope-Seta), the filter flow of aviation fuels is measured at low temperatures across a stainless steel filter. In this method a sample is subjected to a programmed cooling cycle by water-cooled thermoelectric modules, while a pump maintains an oscillating flow at constant rate across the filter. Separated wax crystals cause an increase in pressure which is sensed electronically. There is also the Institute of Petroleum method (IP 16) of determining freezing points.

The freezing point of the jet fuel blend as determined by the IP 16 method has been found to be well below that of the kerosine fraction in the absence of the HCCN component. For instance, a kerosine fraction without the HCCN component has a freezing point of -53.5°C . HCCN alone has a freezing point of -42 to -45°C . However, the same fraction when blended with 2.5% by volume of HCCN has a freezing point of -54°C , when blended with 5% by volume of HCCN has a freezing point of -54.5°C and when blended with 10% by volume of HCCN has a freezing point of -55°C .

Whilst in absolute terms these numbers do not appear significant, in respect of the general risk of waxes crystallising from fuels, these numbers are very significant and reduce the potential risk of blockage of filters and pumps by an order of magnitude. Herein lies the

feature of the invention.

Thus according to a further embodiment, the present invention is a jet fuel blend comprising a major amount of a kerosine fraction boiling within the range of 140° to 250°C and a minor amount of a naphtha fraction produced by the catalytic cracking of heavy gas oil (hereafter "HCCN") which has a distillation range of $T_5 = 165^\circ\text{C}$ to $T_{95} = 210^\circ\text{C}$ and an aromatics content of at least 50 % by volume such that the resultant jet fuel blend has a freezing point below -53.5°C .

A further feature of the present invention is that the HCCN used in the blends to depress the freezing point of jet fuels is substantially a natural component of the petroleum crudes from which the fuel itself is derived. Hence, there are no problems of compatibility problems nor indeed any of the problems associated with external additives.

The jet fuel blends of the present invention may contain in addition any of the conventional additives used in such fuel compositions. For instance, they may contain *inter alia* approved additives such as antioxidants, static dissipators, metal deactivators, lubricity improvers, fuel system icing inhibitors, thermal stability improvers, drag reducing agents, dyes and the like.

The present invention is further illustrated with reference to the following Examples:

EXAMPLES:

A kerosine fraction was taken as the base fuel and was blended with various amounts of HCCN and the various properties measured including the freezing points of the each of the two components and the blends thereof. The freezing points were measured according to the standard Institute of Petroleum (IP16) technique.

The tabulated results below show that in spite of the HCCN fraction having a relatively higher freezing point than the base kerosine and in spite of the density of the HCCN fraction being significantly higher than that of the base kerosine, the eventual result of blending the two is to substantially depress the freezing point of the blend to below the

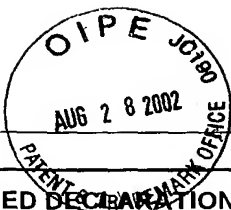
value of the base kerosine without adversely affecting the composition of the fuel to any noticeable degree.

Parameters	Kerosine (%v/v)	HCCN (% v/v)	Amount of HCCN (% v/v) of the total blend with Kerosine			
	100	100	2.5	5.0	7.5	10
Aromatics (% v/v)	17.7	66.0	19.0	19.3	21.5	21.9
Olefins (% v/v)	0.4	3.2	0.7	0.7	0.6	0.6
Distillation IBP(°C)	147.5	83.4	150.2	151	151.1	149
End Point (°C)	243.1	230.0	242.3	240.9	241.0	242.9
Flash Point (°C)	43.0	38.5	42.0	41.5	41.0	41.0
Freeze Point(°C)	-53.5	-44.5	-54.0	-54.5	-55.0	-55.0
KV ₂₀ (mm/s)	3.74	-	-	-	-	-
Density (15°C)	798.2	849.4	799.3	800.8	802.2	803.3

We Claim:

1. A jet fuel blend comprising more than 75 % by volume of a kerosine fraction boiling within the range of 140° to 250°C and a minor amount of a naphtha fraction produced by the catalytic cracking of heavy gas oil (hereafter "HCCN") which has a distillation range of $T_5 = 165^\circ\text{C}$ to $T_{95} = 210^\circ\text{C}$, an aromatics content of at least 50 % by volume such that the resultant jet fuel blend has a freezing point below that of the kerosine prior to blending and that the total aromatic content of the blend is in the range from 15-25% by volume of the total blend.
2. A blend according to Claim 1 wherein the freezing point of the blend is below -53.5°C .
3. A blend according to Claim 1 or 2 wherein the kerosine fraction forming the major component of the blend has a boiling range of $T_5 = 145^\circ\text{C}$ to $T_{95} = 248^\circ\text{C}$.
4. A blend according to any one of the preceding Claims wherein the kerosine fraction forming the major component of the blend has a boiling range of $T_5 = 150^\circ\text{C}$ to $T_{95} = 245^\circ\text{C}$.
5. A blend according to any one of the preceding Claims wherein the amount of the kerosine fraction in the jet fuel blend is in the range of 80-99% by volume of the total blend comprising the kerosine fraction and the HCCN.
6. A blend according to any one of the preceding Claims wherein the HCCN fraction is substantially unhydrorefined and has a boiling range of $T_5 = 165^\circ\text{C}$ to $T_{95} = 210^\circ\text{C}$.
7. A blend according to any one of the preceding Claims wherein the amount of HCCN in the blend is from 0.5 to 15% by volume of the total blend.
8. A fuel composition according to any one of the preceding Claims wherein said composition also contains one or more additives selected from antioxidants, static dissipators, metal deactivators, lubricity improvers, fuel system icing inhibitors, thermal stability improvers, drag reducing agents and dyes.

This invention relates to a jet fuel blend comprising a major amount of a kerosine fraction boiling within the range of 140° to 250°C and a minor amount of a naphtha fraction produced by the catalytic cracking of heavy gas oil which has a distillation range of T₅ = 165°C to T₉₅ = 210°C and an aromatics content of at least 50 % by volume such that the resultant jet fuel blend has a freezing point below that of the kerosine prior to blending. The blends of the present invention can achieve freezing points below -53.5°C.



10099310 082802

US

PCT Applicant's Guide - Volume II - National Chapter - US

Annex US.III, page 1

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to PCT International Applications)

ATTORNEY'S DOCKET NUMBER

P1999S008

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

" JET FUELS WITH IMPROVED FLOW PROPERTIES "

the specification of which (check only one item below):

☐ is attached hereto.☐ was filed as United States application

Serial No.

on

and was amended

on _____ (if applicable).

☒ was filed as PCT international applicationNumber **PCT/EP00/10186**on **17 October 2000**

And was amended under PCT Article 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations. § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY (if PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119	
GB	9925640.6	29 October 1999	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO

Combined Declaration For Patent Application and Power of Attorney (Continued) (Includes Reference to PCT International Applications)				ATTORNEY'S DOCKET NUMBER P1999S008	
I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:					
PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:					
U.S. APPLICATIONS			STATUS (Check One)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO.	PCT FILING DATE	U.S. SERIAL NUMBERS ASSIGNED (if any)			
POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)					
Joseph J. Allocca Registration No. <u>27,766</u>		Estelle C. Bakun Registration No. <u>35,054</u>		Norby L. Foss Registration No. <u>47,571</u> 3	
Send Correspondence to: <u>ExxonMobil Research and Engineering Company</u> (formerly Exxon Research and Engineering Company) <u>P. O. Box 900</u> <u>Annandale, New Jersey 08801-0900</u> <u>U.S.A.</u>				Direct Telephone Calls to: (name and telephone number) <u>Joseph J. Allocca</u> <u>(908) 730-3629</u>	
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
1	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
2	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
3	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
2	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
0	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
4	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application for any patent issuing thereon.					
SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
DATE		DATE		DATE	